Reply to Morel: Cadmium as a micronutrient and macrotoxin in the oceans

Tristan J. Horner[a,1], Renee B. Y. Lee[b], Gideon M. Henderson[b], and Rosalind E. M. Rickaby[b]

[a]Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, MA 02543; and
[b]Department of Earth Sciences, University of Oxford, Oxford OX1 3AN, United Kingdom

We thank François Morel for his interest in our study. Morel states that our conclusions are based on the approximate match between the Cd-isotope composition of cultured bacteria and the fractionation of Cd isotopes seen in seawater (1). This match is only a minor component of our argument, and we welcome the opportunity to reiterate our case.

We propose that the ubiquitous process of Cd homeostasis is likely to outweigh any physiological use of Cd (in place of Zn) in driving oceanic Cd cycling. This is based on the observation that, in our experiments, the Cd-isotopic composition of cultured microbes was independent of the presence/absence of the CdCA1 metalloenzyme (Cd carbonic anhydrase; the only known biochemical function for Cd). Whole-cell Cd-isotope compositions were quantitatively driven by the intracellular sequestration of isotopically light Cd to cell membranes (2). We interpret this sequestration as evidence of microbial Cd homeostasis, which is a ubiquitous and highly conserved process across all forms of life.

Given the tendency of Cd to displace metals from their correct binding site, cytosolic [Cd] must be tightly buffered by organic ligands. In phytoplankton this is achieved by binding with phytochelatin (PC), whereas in Escherichia coli (our cultured microbe), which lack a PC synthase, Cd is bound to glutathione (GSH). GSH is not a perfect analog to PC, although GSH is both functionally analogous to, and a precursor molecule of, PC. Despite the suggestion by Morel otherwise (1), experiments have shown that Cd-PC complexes are exported by plankton when under Cd stress (3). These, and other experiments, have shown that Cd is always internally bound to an excess of PC or PC-like molecules (3, 4). Our data demonstrate that microbial metal homeostasis—in vivo binding of Cd by GSH—causes Cd-isotope fractionation and leads to the retention of inert isotopically light Cd complexes by microorganisms. The magnitude of Cd-isotope fractionation observed during microbial metal homeostasis is consistent with patterns of Cd-isotope fractionation seen in the modern ocean (2).

In culture, almost all plankton will assimilate Cd (5), although this does not prove that Cd is acquired for any specific physiological purpose. Cadmium isotope data for cultured phytoplankton show that isotopically light Cd is internalized (6), even though the species studied lacks the CdCA1 gene (Chlorella spp. and C. reinhardtii; chlorophyte lineage; table S1 in ref. 2). When grown under increasing ambient [Cd^{2+}], the Cd:C of cultured phytoplankton increases monotonically and without apparent limit, regardless of Zn nutritional status (5), implying that uncontrolled "nonspecific uptake" is responsible for determining cellular Cd quotas. Currently, the data do not exist to quantitatively assess the partitioning of Cd to utilization (i.e., through Zn replacement in CdCA1) or homeostasis (e.g., intracellular binding with PC/GSH) in marine microbes, although the gene encoding for CdCA1 is absent in many plankton lineages (table S1 in ref. 2).

Our isotopic data—showing microbial Cd-isotope fractionation by homeostasis following nonspecific "mistaken" uptake—suggest that it is the ubiquitous and essential process of Cd homeostasis that dominates the vertical gradients of [Cd] and Cd-isotope compositions in the modern ocean.

Footnotes

[1]To whom correspondence should be addressed. E-mail: Tristan.Horner@whoi.edu.

Author contributions: T.J.H., R.B.Y.L., G.M.H., and R.E.M.R. wrote the paper.

The authors declare no conflict of interest.

References

1. Morel FMM (2013) The oceanic cadmium cycle: Biological mistake or utilization? *Proc Natl Acad Sci USA* **110**:E1877.
2. Horner TJ, Lee RBY, Henderson GM, Rickaby REM (2013) Nonspecific uptake and homeostasis drive the oceanic cadmium cycle. *Proc Natl Acad Sci USA* **110**(7):2500–2505.
3. Lee JG, Ahner BA, Morel FMM (1996) Export of cadmium and phytochelatin by the marine diatom Thalassiosira weissflogii. *Environ Sci Technol* **30**(6):1814–1821.
4. Price NM, Morel FMM (1990) Cadmium and cobalt substitution for zinc in a marine diatom. *Nature* **344**(6267):658–660.
5. Sunda WG, Huntsman SA (2000) Effect of Zn, Mn, and Fe on Cd accumulation in phytoplankton: Implications for oceanic Cd cycling. *Limnol Oceanogr* **45**(7):1501–1516
6. Lacan F, Francois R, Ji Y, Sherrell RM (2006) Cadmium isotopic composition in the ocean. *Geochim Cosmochim Acta* **70**(20):5104–5118.

Horner, T. J., Lee, R. B. Y., Henderson, G. M., & Rickaby, R. E. M. (2013). Reply to Morel: Cadmium as a micronutrient and macrotoxin in the oceans. *Proceedings of the National Academy of Sciences U.S.A.*, **110**(21), E1878, doi: 10.1073/pnas.1305068110.